

# LABORATORY MEASUREMENT OF THE 2-CENTIMETER, $2_{11}$ - $2_{12}$ , TRANSITION OF NORMAL FORMALDEHYDE AND ITS CARBON-13 AND OXYGEN-18 SPECIES

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## ABSTRACT

The hyperfine components of the  $2_{11}$ - $2_{12}$  transitions of  $\text{H}_2\text{CO}$ ,  $\text{H}_2^{13}\text{CO}$ , and  $\text{H}_2^{18}\text{O}$  have been measured to an accuracy of about 100 Hz.

Receivers at  $\lambda \sim 2$  cm will soon rival or even surpass in sensitivity those currently available at longer wavelengths. There is thus a good prospect that the 2-cm,  $2_{11}$ - $2_{12}$ , formaldehyde rotational line, which has so far been detected in only a few bright sources (Evans, Cheung, and Sloanaker 1969), will become before long a standard astronomical tool. The  $2_{11}$  and  $2_{12}$  levels are appreciably populated by the microwave background, implying that the 2-cm line, like the familiar 6-cm one, should be detectable in the majority of H II regions. On an antenna working at both wavelengths, the 2-cm line has the important advantage over the 6-cm one of a threefold gain in angular resolution.

Very precise laboratory measurements of the hyperfine structure (hfs) of the 6-cm line of several isotopic species of formaldehyde have recently been published (Tucker, Tomasevich, and Thaddeus 1971; hereafter called Paper I); here we report similar measurements of the  $2_{11}$ - $2_{12}$  transition for the isotopic species of greatest astronomical interest:  $\text{H}_2\text{CO}$ ,  $\text{H}_2^{13}\text{CO}$ , and  $\text{H}_2^{18}\text{O}$ . For these species all the coupling constants required to calculate the hfs of any rotational transition are now determined.

Measurements were made with essentially the same beam-maser spectrometer described in Paper I. Samples were not isotopically enriched, monomeric formaldehyde vapor being simply produced by heating a commercial sample of the solid polymer paraformaldehyde.

The observed and best-fit theoretical hyperfine spectra are shown in figure 1; the measured frequencies (or best-fit ones when components are blended) are listed in tables 1 and 2; and the line centers  $\nu_0$  and hyperfine coupling constants derived from the theoretical fit are listed in table 3. The definition of quantum numbers and coupling constants is standard, and may be found in Paper I. The present measurements represent a large improvement in absolute precision over previous work,  $\nu_0$  differing from that of Oka, Hirakawa, and Shimoda (1960) by 60-150 kHz ( $1-3 \text{ km s}^{-1}$ ); the hyperfine splittings for  $\text{H}_2\text{CO}$  are in essential agreement with the previous beam-maser measurements of Thaddeus, Krisher, and Loubser (1964), but are roughly five times as precise.

Figure 2 shows for each isotopic species how the peak frequency of the hyperfine manifold  $\nu_p$  is "pulled" by the blend of hyperfine components (assuming a Gaussian line shape and normal intensities), until at large line width it converges to the line center  $\nu_0$  (see Paper I). The pulling effect amounts at most to about 3 kHz ( $0.06 \text{ km s}^{-1}$ ), and is therefore negligible for most astronomical lines, except possibly the very narrow ones expected in certain dark nebulae.

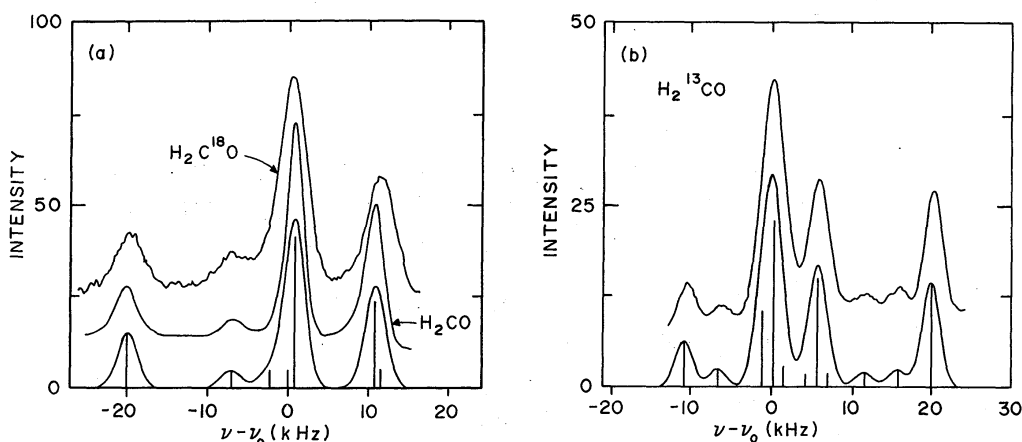


FIG. 1.—(a) *Top two spectra*, observed hfs of the  $2_{11} \rightarrow 2_{12}$  transition of  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{C}^{18}\text{O}$ ; *bottom*, theoretical best-fit hfs for  $\text{H}_2\text{CO}$ . (b) *Top*, most intense observed hfs for  $\text{H}_2^{13}\text{CO}$ ; *bottom*, theoretical best-fit of same (a number of weak satellite lines listed in table 2 fall out of the frequency range in b).

TABLE 1  
HYPERFINE FREQUENCIES OF THE  $2_{11} \rightarrow 2_{12}$   $\text{H}_2\text{CO}$  AND  $\text{H}_2\text{C}^{18}\text{O}$   
TRANSITIONS WITH RESPECT TO LINE CENTERS

TRANSITION* $F \rightarrow F'$	RELATIVE INTENSITY (Theoretical)	$\nu - \nu_0$ (kHz)†	
		$\text{H}_2\text{CO}$	$\text{H}_2\text{C}^{18}\text{O}$
1→1.....	15.00	$-19.97 \pm 0.07$	$-19.97 \pm 0.11$
1→2.....	5.00	$-7.03 \pm 0.10$	$-6.71 \pm 0.25$
2→1.....	5.00	$-2.20 \pm 0.10\dagger$	$-2.32 \pm 0.25\dagger$
3→2.....	5.19	$+0.12 \pm 0.10\dagger$	$-0.29 \pm 0.25\dagger$
3→3.....	41.48	$+0.89 \pm 0.07$	$+0.74 \pm 0.09$
2→2.....	23.15	$+10.74 \pm 0.07$	$+10.95 \pm 0.09$
2→3.....	5.19	$+11.51 \pm 0.10\dagger$	$+11.98 \pm 0.25\dagger$

\*  $F$  refers to the upper level of the transition and  $F'$  to the lower.

† Quoted uncertainty represents the standard deviation of eight measurements.

‡ Calculated frequency.

In the rigid-rotor approximation (highly accurate for all formaldehyde rotational levels of foreseeable astronomical interest) the spin-rotation constant  $C$  of a given nucleus in all levels is determined by three parameters—the diagonal elements  $M_{aa}$ ,  $M_{bb}$ ,  $M_{cc}$  of the spin-rotation tensor. The relation is (Thaddeus *et al.* 1964)

$$C = \sum_a \langle J_a^2 \rangle M_{aa} / J(J+1), \quad (1)$$

where the  $\langle J_a^2 \rangle$  are the rotationally averaged squares of the angular-momentum components along the principal inertial axes. From the present work and Paper I the spin-rotation constants of four levels are known, and hence the three  $M_{aa}$  are overdetermined. A least-squares fit of equation (1) to the data then yields the  $M_{aa}$  listed in table 4. Since the only other hyperfine interaction in these isotopic species—the spin-spin—is also calculable in the rigid-rotor approximation (being simply determined by  $\langle r^{-3} \rangle$ ), the hfs

TABLE 2  
HYPERFINE FREQUENCIES OF THE  $2_{11} \rightarrow 2_{12}$   $\text{H}_2^{13}\text{CO}$   
TRANSITION WITH RESPECT TO LINE CENTER

Transition* $F_1 F \rightarrow F_1' F'$	Relative Intensity (Theoretical)	$\nu - \nu_0^\dagger$ (kHz)
3/2, 1/2-5/2, 3/2 . . . . .	0.69	-111.04
3/2, 3/2-5/2, 3/2 . . . . .	0.13	- 86.76
3/2, 5/2-5/2, 3/2 . . . . .	0.03	- 82.57
3/2, 3/2-5/2, 5/2 . . . . .	1.00	- 78.51
3/2, 5/2-5/2, 7/2 . . . . .	1.48	- 78.38
3/2, 5/2-5/2, 5/2 . . . . .	0.92	- 74.32
3/2, 1/2-3/2, 1/2 . . . . .	3.33	- 53.21
3/2, 1/2-3/2, 3/2 . . . . .	2.65	- 35.16
3/2, 3/2-3/2, 1/2 . . . . .	2.72	- 28.93
3/2, 3/2-3/2, 3/2 . . . . .	6.42	- 10.89
3/2, 5/2-3/2, 3/2 . . . . .	2.58	- 6.69
5/2, 3/2-5/2, 3/2 . . . . .	10.48	- 1.22
5/2, 7/2-5/2, 7/2 . . . . .	22.85	+ 0.20
3/2, 3/2-3/2, 5/2 . . . . .	3.05	+ 1.49
5/2, 7/2-5/2, 5/2 . . . . .	1.83	+ 4.26
3/2, 5/2-3/2, 5/2 . . . . .	14.97	+ 5.69
5/2, 3/2-5/2, 5/2 . . . . .	1.95	+ 7.03
5/2, 5/2-5/2, 3/2 . . . . .	1.98	+ 11.61
5/2, 5/2-5/2, 7/2 . . . . .	2.33	+ 15.80
5/2, 5/2-5/2, 5/2 . . . . .	14.30	+ 19.86
5/2, 3/2-3/2, 1/2 . . . . .	0.62	+ 56.61
5/2, 3/2-3/2, 3/2 . . . . .	0.28	+ 74.65
5/2, 7/2-3/2, 5/2 . . . . .	1.97	+ 84.27
5/2, 5/2-3/2, 3/2 . . . . .	1.38	+ 87.48

\*  $F_1 F$  refers to the upper level of the transition and  $F_1' F'$  to the lower.

<sup>†</sup> Because of blending, all listed frequencies are from the best-fit spectrum; estimated uncertainties are  $\pm 0.15$  kHz.

TABLE 3  
LINE CENTERS AND HYPERFINE COUPLING CONSTANTS

Isotopic Species	Line Center (kHz)	Hyperfine Constant (kHz)
$\text{H}_2\text{CO}$	$14488478.81 \pm 0.08$	$C_H(2_{11}) = 0.19 \pm 0.07$ $C_H(2_{12}) = -2.12 \pm 0.07$ $g_{\text{H}^{14}\text{N}}^{2,2} \langle r_{\text{HH}}^{-3} \rangle = 17.45 \pm 0.16$
$\text{H}_2^{13}\text{CO}$	$13778804.13 \pm 0.15$	$C_C(2_{11}) = 36.01 \pm 0.15$ $C_C(2_{12}) = 29.71 \pm 0.15$ $C_H(2_{11}) = 0.30 \pm 0.09$ $C_H(2_{12}) = -1.94 \pm 0.09$ $g_{\text{H}^{14}\text{N}}^{2,2} \langle r_{\text{HH}}^{-3} \rangle = 17.84 \pm 0.25$ $g_{\text{H}^{15}\text{N}}^{2,2} \langle r_{\text{HC}}^{-3} \rangle = 21.67 \pm 0.28$
$\text{H}_2\text{C}^{18}\text{O}$	$13165954.91 \pm 0.13$	$C_H(2_{11}) = 0.03 \pm 0.15$ $C_H(2_{12}) = -2.23 \pm 0.15$ $g_{\text{H}^{14}\text{N}}^{2,2} \langle r_{\text{HH}}^{-3} \rangle = 17.60 \pm 0.24$

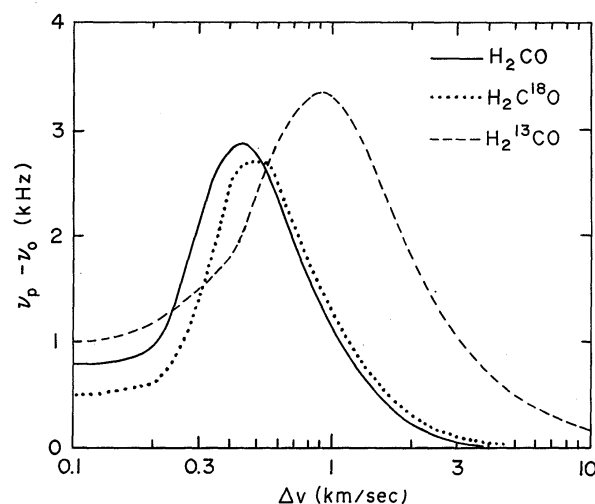


FIG. 2.—Peak frequency of the hyperfine envelope of the  $2_{11} \rightarrow 2_{12}$  transition as a function of line width at half-intensity (in units of velocity:  $\Delta v = c\Delta\nu/\nu$ ).

TABLE 4  
DIAGONAL ELEMENTS OF THE SPIN-ROTATION TENSORS\*

SPECIES NUCLEUS	H <sub>2</sub> CO H	H <sub>2</sub> <sup>13</sup> CO		H <sub>2</sub> C <sup>18</sup> O H
		H	<sup>13</sup> C	
$M_{aa}$ .....	$-3.39 \pm 0.11$	$-3.52 \pm 0.16$	$+127.86 \pm 0.31$	$-3.30 \pm 0.27$
$M_{bb}$ .....	$+1.79 \pm 0.09$	$+1.97 \pm 0.11$	$+19.99 \pm 0.23$	$+1.47 \pm 0.20$
$M_{cc}$ .....	$-2.75 \pm 0.09$	$-2.53 \pm 0.11$	$+7.61 \pm 0.23$	$-2.79 \pm 0.20$

\* In kilohertz.

of any transition may now be calculated. For H<sub>2</sub>CO and H<sub>2</sub><sup>13</sup>CO the rotation and centrifugal distortion parameters are now very precisely known from the work of Nerf (1972, this issue), and for these species the hyperfine frequencies may therefore be calculated absolutely to high accuracy. We have recently detected the 1-cm  $3_{13} \rightarrow 3_{12}$  transition of H<sub>2</sub>CO with our beam maser, and the measured frequencies fall within a few parts in  $10^8$  of the predicted frequencies.

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